REMARKS

I. STATUS OF THE CLAIMS

Claims 1-21 and 23 are currently pending.

Applicant has amended the specification to incorporate the language of original claim 19 in accordance with M.P.E.P. § 2163.06. Accordingly, no new matter has been added.

Applicant has added new claim 23, which recites "wherein the non-consumable solids constitute from 8% to 20% by weight of the aqueous suspension of the non-consumable solids in the aqueous medium." Support for this amendment is found in the specification, for example in original claim 19 and Example 1 (disclosing 8%). M.P.E.P. § 2163.05 (*citing, In re Wertheim*, 191 U.S.P.Q. 90, 98 (C.C.P.A. 1976) (holding that a claim reciting a range of 35-60% has written description support in a specification disclosing a range of 25-60% with an example of 36% and 50%)). Just as in *In re Wertheim*, Applicant's new claim is fully supported by the specification's disclosure of 0.5% to 20% and an example with 8% by weight of the aqueous suspension of the non-consumable solids in the aqueous medium.

Applicant respectfully acknowledges that the Office has withdrawn the rejections under 35 U.S.C. § 103(a) over Kosin et al. (U.S. Patent No. 4,888,160); under 35 U.S.C. § 103(a) over Kosin et al. in view of Bleakley I (EP 0 604 095); under 35 U.S.C. § 103(a) over Ota et al. (U.S. Patent No. 4,824,654) in view of Bleakley II (U.S. Patent No. 5,342,600) alone or further in view of Kosin et al.; and under 35 U.S.C. § 103(a) over

Ota et al. in view of Bleakley II either alone or further in view of Kosin, and further in view of Bleakley I.

II. SECTION 103(a) REJECTION

The Office has rejected claims 1-21 under 35 U.S.C. § 103(a) as unpatentable over Matthews et al. (U.S. Patent No. 5,679,220) for the reasons disclosed at pages 2 through 4 of the Final Office Action. Applicant respectfully traverses this rejection for at least the reasons presented below.

The claimed invention, as recited in *e.g.*, claim 1, is directed to a method of continuously producing a product comprising precipitated calcium carbonate. The method comprises continuously delivering an aqueous suspension of a calcium ion source and carbon dioxide into single-pass channel comprising a series of at least two static in-line mixers, and then continuously extracting from the channel precipitated calcium carbonate suspended in an aqueous medium, produced by reaction of the calcium ion source and carbon dioxide in the channel.

Applicant's invention is not obvious over Matthews et al. As an initial matter, a *prima facie* case of obviousness requires three basic criteria to be met. M.P.E.P. § 2142. First, the Office must establish that Matthews et al. teaches or suggests all the claim limitations. *See* M.P.E.P. § 2143.03. Second, the Office must establish that some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, exists to modify the reference. *See* M.P.E.P. § 2143.01. Finally, the Office must establish a reasonable expectation of success from the required modification. *See* M.P.E.P. § 2143.02. In the present case,

at a minimum, Matthews et al. does not teach or suggest all the claim limitations nor is there a suggestion or motivation in the art to modify the teachings of Matthews et al.

The Office asserts that Matthews et al. discloses "the resulting mixture may then immediately be sent through in-line mixers, such as static in-line mixers. . . ." Final Office Action at 2. Applicant respectfully disagrees with the Office's characterization of Matthews et al. Specifically, Matthews et al. does not expressly or inherently disclose the use of ***static*** in-line mixers, as required by all of the claims. Matthews et al. merely discloses the possible use of general in-line mixers. Col. 4, lines 58-60, col. 7, lines 35-39.

"In-line mixer" is a much broader term than "static in-line mixer." Applicant submits that the Office has already acknowledged this fact when it used the phrase "such as." Final Office Action at 2. It is well-known in the art that there are rotary mixers and pumps are common in-line mixers. *See e.g.,* Perry's Chemical Engineers' Handbook, 21-57 to 21-59 (6th ed. 1984) (copy enclosed). In Perry's, static in-line mixers, such as packed tubes, are the last options considered for its discussion of line mixers. *Id.* In addition, when discussing continuous processes, ***static*** in-line mixers are treated as an after-thought. *Id.* at 19-19 to 19-23. Accordingly, Applicant submits that a person of ordinary skill in the art would not believe the disclosure of "in-line mixers" to be an express disclosure of "static in-line mixers."

In addition, Matthews et al. is not an inherent disclosure of a static in-line mixer. *Akzo N.V. v. U.S. Int'l Trade Comm.*, 1 U.S.P.Q.2d 1241, 1425 (Fed. Cir. 1986). In Akzo, the Federal Circuit affirmed the ITC's determination that the claim, reciting the use of "at least 98% concentrated sulfuric acid," was not invalidated by a reference

disclosing the use "sulfuric acid." *Id.* While the term "sulfuric acid" encompasses "at least 98% concentrated sulfuric acid," the evidence established that a person of ordinary skill in the art would not immediately assume "sulfuric acid" meant "at least 98% concentrated sulfuric acid" only that it could mean that. *Id.* Accordingly, like Akzo, the mere disclosure of "in-line mixers" is not enough to render claims to "static in-line mixers" unpatentable.

Moreover, there is no motivation provided for a person of ordinary skill in the art to select a static in-line mixer in view of the fact that (1) Matthews et al. teaches that the mere passing of fluid though a tube creates enough turbulence (col. 4, lines 58-60, col. 6, lines 43-45) and (2) Perry's teaches that static in-line mixers create significant pressure drop. (Perry's at 19-22). Thus, the requisite motivation to modify the teachings of Matthews et al. is not present and a *prima facie* case of obviousness has not been established. *See* M.P.E.P. § 2143.01.

Applicant further submits that Matthews et al. does not teach all of the elements of claim 23, including the one reciting "wherein the non-consumable solids constitute from 8% to 20% by weight of the aqueous suspension of the non-consumable solids in the aqueous medium." Matthews et al. teaches that the weight of the fibers may "not [be] greater than about 5%." Col. 4, lines 1-4. Since 8% is greater than about 5%, Matthews et al. does not teach or suggest this limitation. Moreover, a person of ordinary skill in the art would recognize that Matthews et al. teaches away from this limitation. *See* M.P.E.P. § 2145 (there is no obviousness, where the prior art teaches away). Specifically, Matthews et al. discloses that an amount in excess of about 5%

results in significant deficiencies in the process. Col. 4, lines 4-8. Accordingly, a person of ordinary skill in the art would not be motivated to modify Matthews et al.'s teachings.

Since Matthew et al. does not teach or suggest a "static in-line mixer" and teaches away from a range of "8% to 20% by weight", a *prima facie* case of obviousness has not been established. M.P.E.P. § 2142. Accordingly, the rejection under Section 103 has been overcome and Applicant respectfully requests it be withdrawn.

III. CONCLUSION

Applicant respectfully requests that this Amendment under 37 C.F.R. § 1.116 be entered by the Examiner, placing claim 23 in condition for allowance. Applicants submits that the proposed amendments of claim 23 does not raise new issues or necessitate the undertaking of any additional search of the art by the Examiner, since all of the elements and their relationships claimed were either earlier claimed or inherent in the claims, as examined. Therefore, this Amendment should allow for immediate action by the Examiner.

Furthermore, Applicant respectfully points out that the final action by the Examiner presented some new arguments as to the application of the art against the claimed invention. It is respectfully submitted that the entering of the Amendment would allow the Applicant to reply to the final rejection and place the application in condition for allowance.

Finally, Applicant submits that the entry of the amendment would place the application in better form for appeal, should the Examiner dispute the patentability of the pending claims.

In view of the foregoing remarks, Applicant submits that this claimed invention, as amended, is neither anticipated nor rendered obvious in view of the prior art references cited against this application. Applicant therefore requests the entry of this Amendment, the Examiner's reconsideration of the application, and the timely allowance of the pending claims.

Please grant any extensions of time required to enter this response and charge any additional required fees to our deposit account no. 06-0916.

Respectfully submitted,

FINNEGAN, HENDERSON, FARABOW,
GARRETT & DUNNER, L.L.P.

Dated: December 17, 2004

By: Anthony A. Hartmann
Anthony A. Hartmann
Reg. No. 43,662

Attachment: Perry's Chemical Engineers' Handbook, 19-19 to 19-23 & 21-57 to 21-59 (6th ed. 1984)

PERRY'S CHEMICAL ENGINEERS' HANDBOOK

SIXTH EDITION

McGraw-Hill Book Company

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St. Louis
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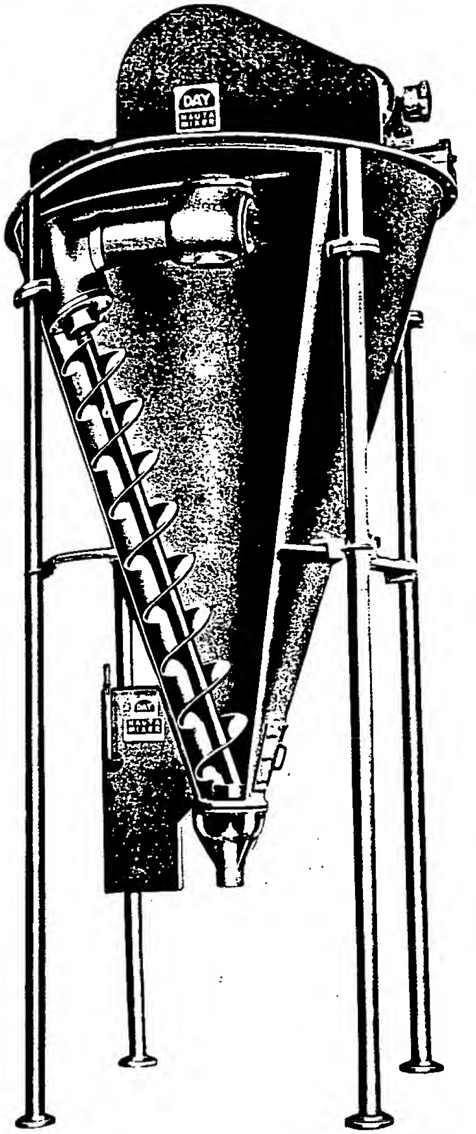

FIG. 19-23 Nauta mixer. *(Day Mixing.)*

Standard muller mixers range in capacity from a fraction of a cubic foot to more than 1.8 m^3 (60 ft^3), with power requirements ranging from 0.2 to 56 kW (⅓ to 75 hp). A continuous muller design employs two intersecting and communicating cribs, each with its own mullers and plows. At the point of intersection of the two crib bodies, the outside plows give an approximately equal exchange of material from one crib to the other, but material builds up in the first crib until the feed rate and the discharge rate of material from the gate in the second crib are equal. The residence time is regulated by adjusting the outlet gate.

CONTINUOUS MIXERS

Single-Screw Extruders The single-screw extruder is frequently used as a mixing device in the plastics industry. Stabilizers, color concentrates, etc., may be compounded with granular raw polymer, melted, and extruded into pellets, sheet, or rod. Detailed descriptions of extruders and procedures for calculating the degree of mixing

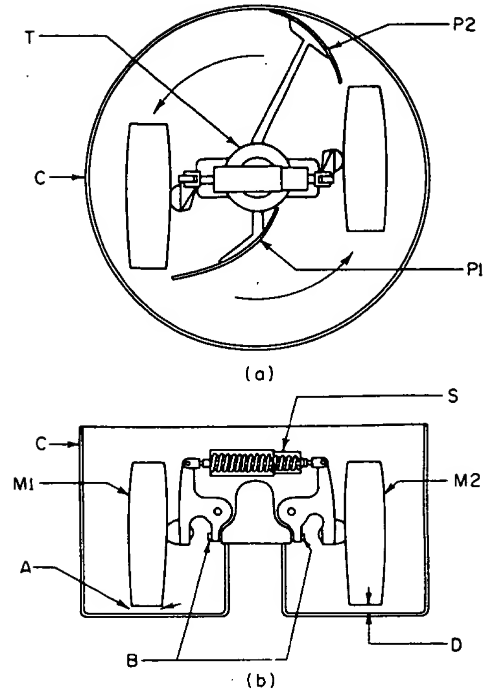

FIG. 19-24 Pan muller. (*a*) Plan view. (*b*) Sectional elevation. [*Bullock*, Chem. Eng. Prog., *51, 243 (1955), by permission.*]

attainable are available elsewhere (Irving and Saxton, op. cit.; and Paton et al., in Bernhardt, *Processing of Thermoplastic Materials*, Reinhold, New York, 1967, chap. 4). In essence a "circulating" movement is achieved by working against a discharge pressure such that there is a pressure flow opposite to the forwarding drag flow of the screw. Single-screw extruders can be equipped with large gears and thrust bearings to operate with high torque and high power input to the material.

Rietz Extructor This extruder, shown schematically in Fig. 19-25, has orifice plates and baffles along the vessel. The rotor carries multiple blades with a forward pitch, generating the head for extrusion through the orifice plates as well as battering the material to break up agglomerates between the baffles. Typical applications include wet granulation of pharmaceuticals, blending color in bar soap, and mixing and extruding cellulose materials. The Extructor is available in rotor diameters up to 600 mm (24 in) and in a power range of 5 to 112 kW (7 to 150 hp).

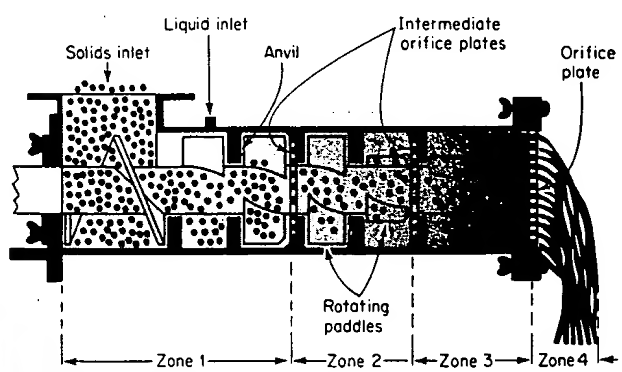

FIG. 19-25 Ritez Extructor. *(Bepex Corporation.)*

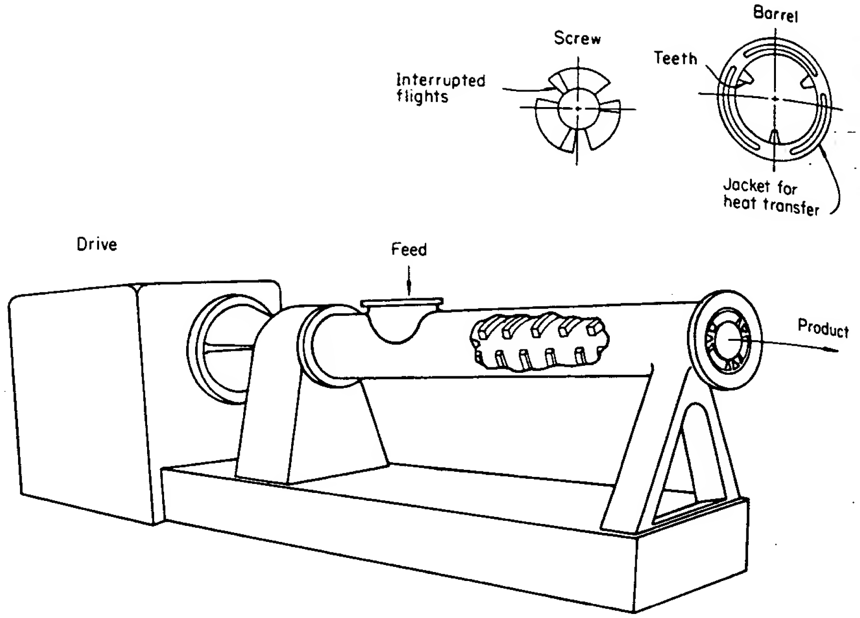

FIG. 19-26 Ko-Kneader. *(Baker Perkins Inc.)*

Baker Perkins Ko-Kneader Depicted in Fig. 19-26, this extruder is a single-screw mixer with an interrupted flight and with three rows of teeth protruding inward from the barrel wall. The screw is both rotated and reciprocated, with the stationary teeth passing through the interruptions in the thread of the screw. In essence, each tooth serves as a mixer to stir the material in the flight channel once each rotation. Thus it is possible to achieve a high degree of mixing in a relatively short retention time. Ko-Kneaders are available in nominal diameters ranging from 50 to 600 mm (2 to 24 in), with power up to 1100 kW (1500 hp). Table 19-3 shows typical uses and performance data for a 100-mm (4-in) Ko-Kneader.

Transfer-Mix This mixer (Sterling Extruder Corp.) is similar to a single-screw extruder except that both the screw and the barrel are divided into frustoconical sections, and both have helical channels. The helical channels are of opposite hand. As the screw turns, material moves forward in both helices but is also partially peeled off one into the other. This exchange circumvents the poor mixing occurring within the flights of a conventional single-screw extruder.

Baker Perkins Rotofeed This extruder (Fig. 19-27) is a light-duty mixer useful for forming pastes and slurries or for preblending doughs or resinous materials. Powdery material enters the top port, while liquid can be injected through teeth projecting into the conical screw section. The large disengaging area at the charging end makes the unit particularly effective as a continuous deaerating device.

Twin-Screw Continuous Mixers Twin-screw continuous mixers may be either tangential or intermeshing. Tangential designs permit larger shaft diameters and higher energy inputs. The blades can be run at different speeds to cause material movement from one barrel section to the other. Intermeshing screws provide the additional shear surface of blade against blade. This feature enables the blades to be self-wiping. Twin-screw machines are used for melting, mixing, coloring, and homogenizing of different polymers. Blending operations requiring incorporation of fillers, reinforcing agents, glass fibers, etc., can be carried out continuously in such mixers.

ZSK Twin-Screw Machines These mixers (Werner & Pfleiderer Corp.) are equipped with corotating screws which are individually made up of different screw and kneading elements slipped onto shafts (Fig. 19-28). The screws are self-wiping and produce positive conveyance of material. By different arrangements of the screws and kneading elements the residence-time distribution can be adjusted and controlled pressure buildup and shear rate can be achieved. Owing to rather shallow flights, heat-exchange and devolatilizing

TABLE 19-3 Ko-Kneader Performance Data*

Compound mixed	Output		Residence time, s	Net energy input	
	kg/h	lb/h		kWh/kg	(hp·h)/lb
Carbon electrode paste	500	1100	50	0.01	0.006
Propellants	400	880	100	0.02	0.012
Kaolin clay	750	1650	60	0.10	0.061
Battery paste	1000	2200	60	0.01	0.006
Polyethylene					
Low-density	750	1650	20	0.10	0.061
High-density	600	1320	20	0.13	0.079
Polyvinyl chloride					
Flexible	1240	2730	20	0.06	0.037
Rigid	750	1650	30	0.10	0.061
Polypropylene	570	1250	20	0.13	0.079

*Provided by Baker Perkins Inc. for a 100-mm- (4-in-) diameter Ko-Kneader.

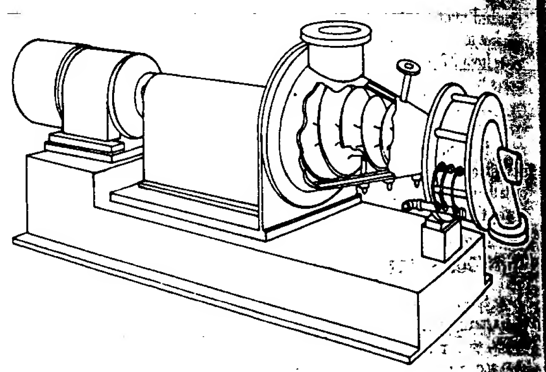

FIG. 19-27 Rotofeed mixer. *(Baker Perkins Inc.)*

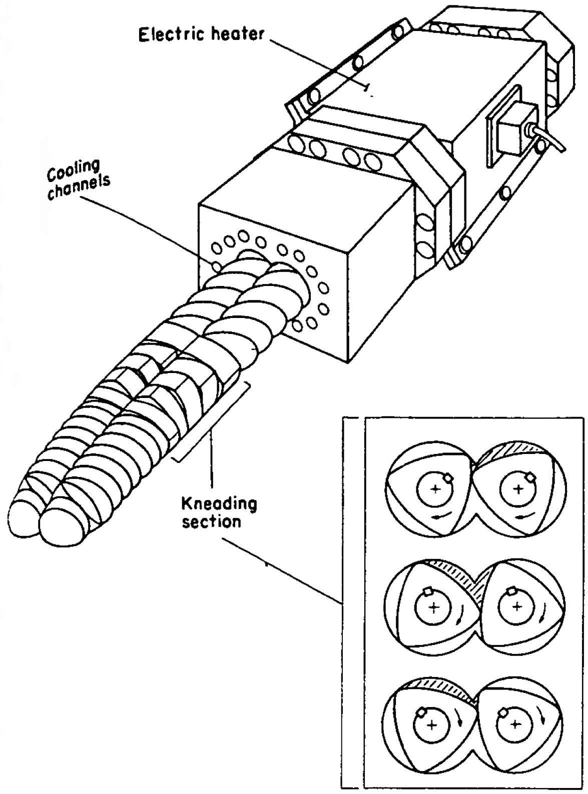

FIG. 19-28 ZSK twin-screw compounding extruder. *(Werner & Pfleiderer Corp.)*

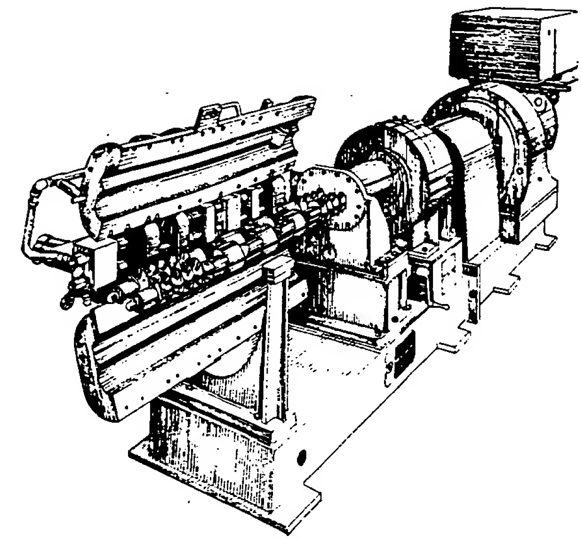

FIG. 19-29 M-P multipurpose mixer. *(Baker Perkins Inc.)*

processes can be carried out, made feasible by the continuous renewal of surfaces of the material stock. The housing of the processing section is made up of different barrel sections, which can be arranged in different numbers according to the process to be performed. The barrel sections are jacketed; they can be electrically heated, vapor-heated, or cooled by water or oil. These mixers are available with a maximum length-to-diameter ratio of 36 in sizes of 28 to 300 mm (1.1 to 12 in). They operate at speeds up to 300 r/min, requiring up to 3000 kW (4000 hp).

Multipurpose (M-P) Mixer This somewhat similar mixer (Baker Perkins Inc.) is shown in Fig. 19-29. Each pair of agitator elements causes an alternate compression and expansion twice each revolution.

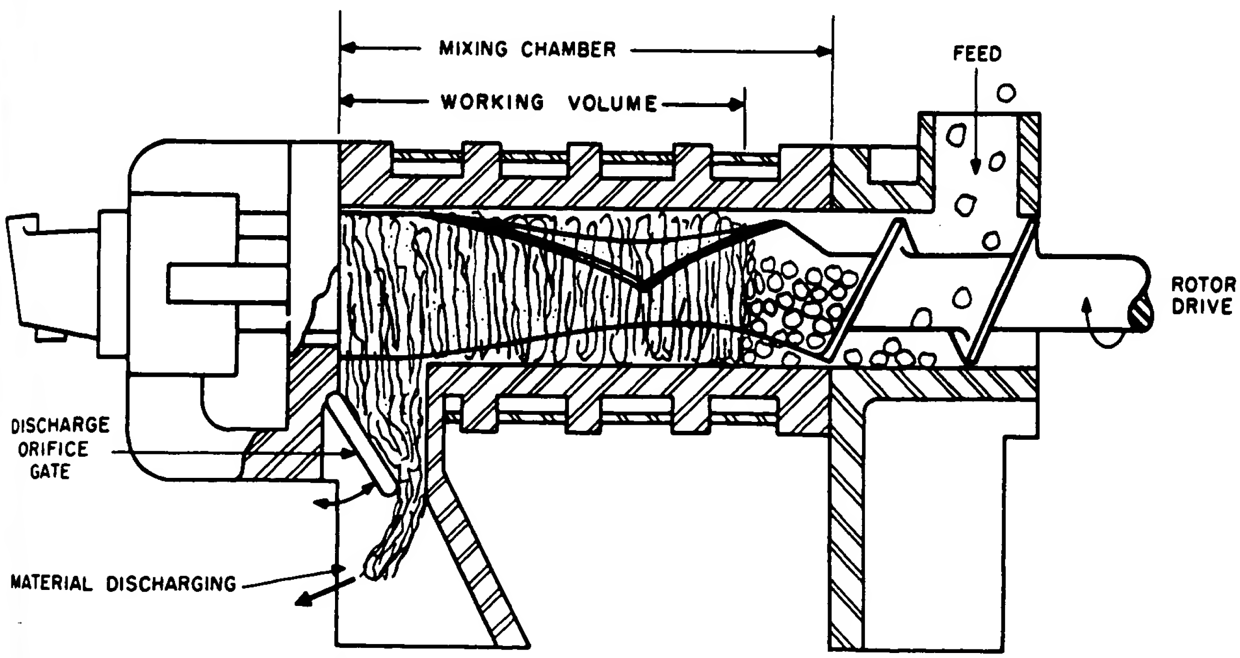

FIG. 19-30 Farrel continuous mixer. *(Farrel Co.)*

Staggering the lens-shaped elements along the shaft squeezes the material from the compression phase of one agitator pair to the expansion phase of an adjoining agitator pair. The land area at the blade tips provides a region of intense shear analogous to the nip of a two-roll mill. These multipurpose mixers have been built in sizes of 30 to 890 mm (1.2 to 35 in), applying up to 1500 kW (2000 hp). The agitators can be cored to double the heat-transfer area. The blades wipe each other as well as wiping the barrel walls, improving heat transfer and preventing any dead spots.

Farrel Continuous Mixer This mixer (Fig. 19-30) consists of rotors similar in cross section to the Banbury batch mixer. The first section of the rotor acts as a screw conveyor, propelling the feed ingredients to the mixing section. The mixing action is a combination of intensive shear, between rotor and chamber wall, kneading between the rotors, and a rolling action of the material itself. The amount and quality of mixing are controlled by adjustment of speed, feed rates, and discharge-orifice opening. Units are available in five sizes with mixing-chamber volumes ranging up to 0.12 m^3 (4.2 ft^3). At 200 r/min, the power range is 5 to 2200 kW (7 to 3000 hp).

Miscellaneous Continuous Mixers

Trough-and-Screw Mixers These mixers usually consist of single or twin rotors which continually turn the feed material over as it progresses toward the discharge end. Some have been designed with extensive heat-transfer area. The continuous-screw **Holo-Flite Processor** (Western Precipitation Division, Joy Manufacturing Company) is used primarily for heat transfer, since the hollow screws present extended surface without contributing much shear. Two or four screws may be used. Bethlehem Corp.'s **Porcupine Processor** (Fig. 19-31) also has heat-transfer media going through the flights of the rotor, but the agitator flights are cut to provide a folding action on the process mass. Breaker-bar assemblies, consisting of fingers extending toward the shaft, are frequently used to improve agitation.

Pug Mills A pug mill contains one or two shafts fitted with short, heavy paddles, mounted in a cylinder or trough which holds the material being processed. In two-shaft mills the shafts are parallel and may be horizontal or vertical. The paddles may or may not intermesh. Clearances are wide so that there is considerable mass mixing. Unmixed or partially mixed ingredients are fed at one end of the machine, which is usually totally enclosed. The paddles push the material forward as they cut through it, and carry the charge toward the discharge end as it is mixed. Product may discharge through one or two open ports or through one or more extrusion nozzles which give roughly shaped, continuous strips. Automatic cutters may be used to make blocks from the strips. Pug mills are most used for mixing mineral and clay products.

Kneadermaster This mixer (Patterson Industries, Inc.) is an adaptation of a sigma-blade mixer for continuous operation. Each two pairs of blades establish a mixing zone, the first pair pushing materials toward the discharge end of the trough and the second pair pushing them back. Forwarding to the next zone is by displacement with more feed material. Control of mixing intensity is by variation in rotor speed. Cored blades supplement the heat-transfer area of the jacketed trough.

Motionless Mixers A fairly recent development in continuous viscous mixing involves the use of stationary shaped diverters inside conduits which force the fluid media to mix themselves through a progression of divisions and recombinations, forming striations of ever-decreasing thickness until uniformity is achieved. Simple diverters, such as the Kenics static mixer (Chemineer, Inc.; Fig. 19-32), provide 2^n layerings per n diverters.

The power consumed by a motionless mixer in producing the mixing action is simply that delivered by a pump to the fluid which it moves against the resistance of the diverter conduit. For a given rate of pumping, it is substantially proportional to that resistance. When the diverter consists of several passageways, as in the Sulzer static mixer (Koch Engineering Co., Inc.) shown in Fig. 19-33, the number of layerings (hence, the rate of mixing) per diverter is increased, but at the expense of a higher pressure drop. The pressure drop, usually expressed as a multiple K of that of the empty duct, is strongly dependent upon the hydraulic radius of the divided flow passageway. The value of K, obtainable from the mixer supplier, can range from 6 to several hundred, depending on the Reynolds number and the geometry of the mixer.

Motionless mixers continuously interchange fluid elements between the walls and the center of the conduit, thereby providing enhanced heat transfer and relatively uniform residence times.

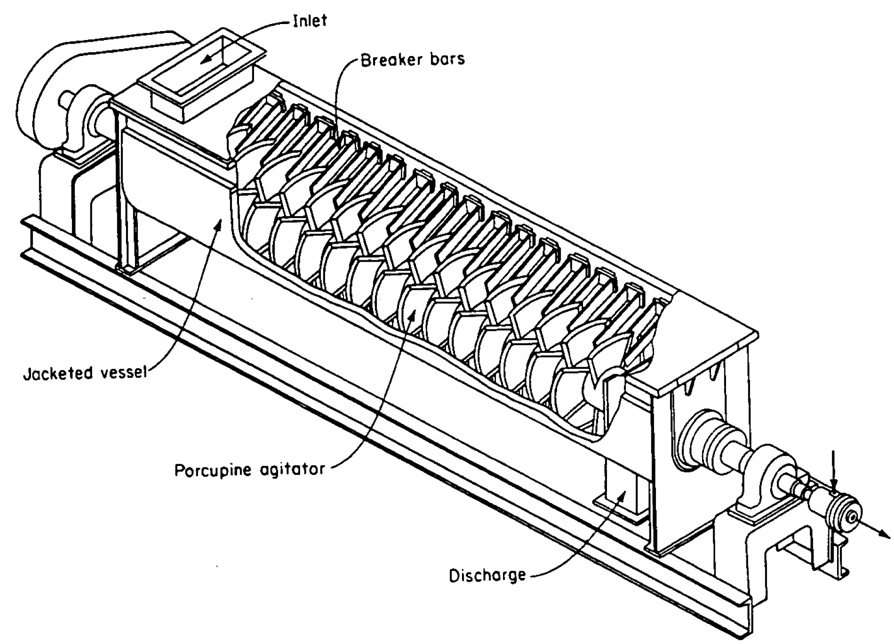

FIG. 19-31 Porcupine Processor. *(Bethlehem Corp.)*

FIG. 19-32 Kenics static mixer. *(Chemineer, Inc.)*

PROCESS DESIGN CONSIDERATIONS

Scaling Up Mixing Performance

Scale-Up of Batch Mixers The prime basis of scale-up of batch mixers has been equal power per unit volume, although the most desirable practical criterion is equal blending per unit time. As size is increased, mechanical-design requirements may limit the larger mixer to lower agitator speeds; if so, blend times will be longer in the larger mixer than in the smaller prototype. If the power is high, the lower surface-to-volume ratio as size is increased may make temperature buildup a limiting factor. Since the impeller in a paste mixer generally comes close to the vessel wall, it is not possible to add cooling coils. In some instances, the impeller blades can be cored for additional heat-transfer area.

Experience with double-arm mixers indicates that power is proportional to the product of blade radius, blade-wing depth, trough length, and average of the speeds of the two blades (Irving and Saxton, loc. cit.). The mixing time scales up inversely with blade speed. Goodness of mixing is dependent primarily on the number of revolutions that the blades have made. As indicated previously, the minimum possible mixing time may become dependent on heat-transfer rate.

Frequently, the physical properties of a paste vary considerably during the mixing cycle. Even if one knew exactly how power depended upon density and viscosity, it might be better to predict the requirements for a large paste mixer from the power-time curve observed in the prototype mixer rather than to try to calculate or measure all intermediate properties during the processing sequence (i.e., the prototype mixer may be the best instrument to use to measure the effective viscosity).

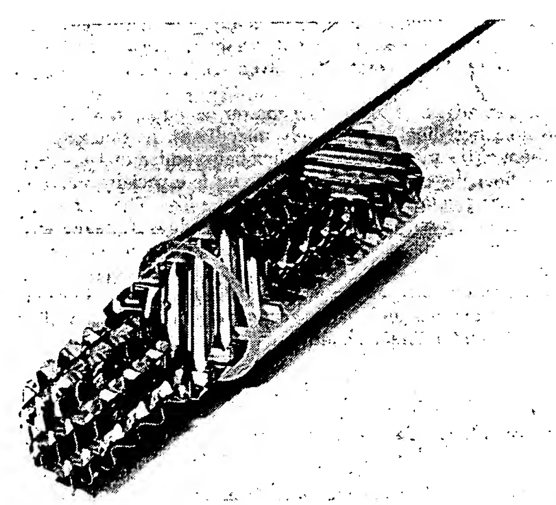

FIG. 19-33 Sulzer static mixer. *(Koch Engineering Co., Inc.)*

Scale-Up of Continuous Mixers Although scaling up on the basis of constant power per unit feed rate [kWh/kg or (hp·h)/lb] is usually a good first estimate, several other factors may have to be considered. As the equipment scale is increased, geometric similarity being at least approximated, there is a loss in surface-to-volume ratio. As size is increased, changing shear rate or length-to-diameter ratio may be required because of equipment-fabrication limitations. Furthermore, even if a reliable method of scaling up power exists, the determination of net power in small-scale test equipment is frequently difficult and inaccurate because of fairly large no-load power.

As a matter of fact, geometrical similarity usually cannot be maintained exactly as the size of the model is increased. In single-screw extruders, for example, channel depth in the flights cannot be increased in proportion to screw diameter because the distribution of heat generated by friction at the barrel wall requires more time as channel depth becomes greater. With constant retention time, therefore, nonhomogeneous product would be discharged from the scaled-up model. As the result of the departure from geometrical similarity, the throughput rate of single-screw extruders scales up with diameter to the power 2.0 to 2.5 (instead of diameter cubed) at constant length-to-diameter ratio and screw speed. The Ko-Kneader (Fig. 19-26) can be held geometrically similar, however, and its throughput rate is scaled up with the cube of diameter at constant speed.

The throughput rate of intermeshing twin-screw extruders (Fig. 19-28) and the Farrel continuous mixer (Fig. 19-30) is scaled up with diameter to about the 2.6 power. The production capacity of the M-P mixer (Fig. 19-29) is scaled up as the cube of diameter since geometry, shear rate, residence time, and power input per unit volume all can be held constant.

Residence-time distributions. For flow through a conduit, the extent of axial dispersion can be characterized either by an axial-diffusion coefficient or by analogy to a number of well-mixed stages in series. Retention time can control the performance of a mixing system. As the number of apparent stages increases, there is greater assurance that all the material will have the required residence time. Under conditions requiring uniform retention time, it is imperative that the feed streams be fed in the correct ratio on a time scale much shorter than the average residence time of the mixer; otherwise, a perturbation in the feed will produce a comparable perturbation in the product. The mixing impellers in continuous mixers can be designed to cover the full range from minimum axial mixing (plug flow) to maximum (to damp out feed irregularities). Residence-time distributions and effective Peclet numbers have been determined for a wide variety of twin-screw configurations [Todd and Irving, *Chem. Eng. Prog.*, 65(9), 84 (1969)]. Conventional single-screw extruder mixers have Peclet numbers about equal to the length-to-diameter ratio, or an equivalent number of stages equal to one-half of that.

Heating and Cooling Mixers

Heat Transfer Pastes are often heated or cooled by heat transfer through the walls of the container or hollow mixing arms. Good agitation, a large ratio of transfer surface to mixer volume, and frequent removal of material from the surface are essential for high rates of heat transfer. Sometimes evaporation of part of the mix is used for cooling.

In most mixers, the metal wall has a negligible thermal resistance. The paste film, however, usually has high resistance. It is important, therefore, while minimizing the resistance of the heating or cooling medium, to move the paste up to and away from the smooth wall surface as steadily and rapidly as possible. This is best achieved by having the paste flow so as to follow a close-fitting scraper which wipes the film from the wall with each rotation. Typical overall heat-transfer coefficients are between 25 and 200 $J/(m^2 \cdot s \cdot K)$ [4 to 35 $Btu/(h \cdot ft^2 \cdot °F)$].

Heating Methods The most economical heating method varies with plant location and available facilities. Direct firing is rarely used, since it does not permit good surface-temperature control and may cause scorching of the material on the vessel walls. Steam heating is the most widely used method. It is economical, safe, and easily

Symbol	Definition	SI units	U.S. customary units
ϵ	Fraction void volume in packed section		
θ	Time of contact	s	h
θ_C	Time between coalescences	s	h
θ_F	Time of drop formation	s	h
λ	Eigenvalue		
μ	Viscosity	Pa·s	lbm/(ft·h)
μ'	Viscosity	Pa·s	cP
ν	Coalescence frequency, fraction of drops coalescing per time	L/s	L/h
π	3.1416		
ρ	Density	kg/m³	lbm/ft³
Σ	Summation		
σ	Interfacial tension	N/m	lbf/ft
σ'	Interfacial tension	N/m	dyn/cm
ϕ	Volume fraction of a liquid in a vessel or extractor's void volume		
ω	Vibration frequency for oscillating drops	L/s	L/h
	Additional subscripts		
av	Average		
C	Continuous phase		
D	Dispersed phase		
E	Extract		
F	Flooding		
H	Heavy liquid		
L	Light liquid		
max	Maximum		
o	Organic		
plug	Plug flow		
R	Raffinate		
w	Water or aqueous liquid		
1	Concentrated end		
2	Dilute end		

Introduction Insoluble liquids may be brought into direct contact to cause transfer of dissolved substances, to allow transfer of heat, and to promote chemical reaction. This subsection concerns the design and selection of equipment used for conducting this type of liquid-liquid contact operation.

Objectives There are four principal purposes of operations involving the direct contact of immiscible liquids. The purpose of a particular contact operation may involve any one or any combination of the following objectives:

1. *Separation of components in solution.* This includes the ordinary objectives of liquid extraction, in which the constituents of a solution are separated by causing their unequal distribution between two insoluble liquids, the washing of a liquid with another to remove small amounts of a dissolved impurity, and the like. The theoretical principles governing the phase relationships, material balances, and number of ideal stages or transfer units required to bring about the desired changes are to be found in Sec. 15. Design of equipment is based on the quantities of liquids and the efficiency and operating characteristics of the type of equipment selected.

2. *Chemical reaction.* The reactants may be the liquids themselves, or they may be dissolved in the insoluble liquids. The kinetics of this type of reaction is treated in Sec. 4.

3. *Cooling or heating a liquid by direct contact with another.* Although liquid-liquid-contact operations have not been used widely for heat transfer alone, this technique is one of increasing interest. Applications also include cases in which chemical reaction or liquid extraction occurs simultaneously.

4. *Creating permanent emulsions.* The objective is to disperse one liquid within another in such finely divided form that separation by settling either does not occur or occurs extremely slowly. The purpose is to prepare the emulsion. Neither extraction nor chemical reaction between the liquids is ordinarily sought.

Liquid-liquid contacting equipment may be generally classified into two categories: **stagewise** and **continuous (differential)** contact.

STAGEWISE EQUIPMENT: MIXER-SETTLERS

The function of a stage is to contact the liquids, allow equilibrium to be approached, and to make a mechanical separation of the liquids. The contacting and separating correspond to mixing the liquids, and settling the resulting dispersion; so these devices are usually called **mixer-settlers.** The operation may be carried out in batch fashion or with continuous flow. If batch, it is likely that the same vessel will serve for both mixing and settling, whereas if continuous, separate vessels are usually but not always used.

Mixer-Settler Equipment The equipment for extraction or chemical reaction may be classified as follows:

- I. Mixers
  - A. Flow or line mixers
    1. Mechanical agitation
    2. No mechanical agitation
  - B. Agitated vessels
    1. Mechanical agitation
    2. Gas agitation
- II. Settlers
  - A. Nonmechanical
    1. Gravity
    2. Centrifugal (cyclones)
  - B. Mechanical (centrifuges)
  - C. Settler auxiliaries
    1. Coalescers
    2. Separator membranes
    3. Electrostatic equipment

In principle, at least, any mixer may be coupled with any settler to provide the complete stage. There are several combinations which are especially popular. Continuously operated devices usually, but not always, place the mixing and settling functions in separate vessels. Batch-operated devices may use the same vessel alternately for the separate functions.

Flow or Line Mixers

Definition Flow or line mixers are devices through which the liquids to be contacted are passed, characterized principally by the very small time of contact for the liquids. They are used only for continuous operations or semibatch (in which one liquid flows continuously and the other is continuously recycled). If holding time is required for extraction or reaction, it must be provided by passing the mixed liquids through a vessel of the necessary volume. This may be a long pipe of large diameter, sometimes fitted with segmental baffles, but frequently the settler which follows the mixer serves. The energy for mixing and dispersing usually comes from pressure drop resulting from flow.

There are many types, and only the most important can be mentioned here. [See also Hunter, in Dunstan (ed.), *Science of Petroleum*, vol. 3, Oxford, New York, 1938, pp. 1779–1797.] They are used fairly extensively in treating petroleum distillates, in vegetable-oil refining, in extraction of phenol-bearing coke-oven liquors, in some metal extractions, and the like. Kalichevsky and Kobe (*Petroleum Refining with Chemicals*, Elsevier, New York, 1956) discuss detailed application in the refining of petroleum.

Jet Mixers These depend upon impingement of one liquid on the other to obtain a dispersion, and one of the liquids is pumped through a small nozzle or orifice into a flowing stream of the other. Both liquids are pumped. They can be used successfully only for liquids of low interfacial tension. See Fig. 21-76 and also Hunter and Nash [*Ind. Chem.*, 9, 245, 263, 317 (1933)]. Treybal (*Liquid Extraction*, 2d ed., McGraw-Hill, New York, 1963) describes a more elab-

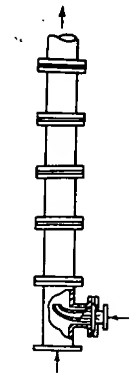

FIG. 21-76 Elbow jet mixer with orifice column. (*Treybal,* Liquid Extraction, *2d ed., McGraw-Hill, New York, 1963, with permission.*)

orate device. For a study of the extraction of antibiotics with jet mixers, see Anneskova and Boiko, *Med. Prom. SSSR,* 13(5), 26 (1959). Insonation with ultrasound of a toluene-water mixture during methanol extraction with a simple jet mixer improves the rate of mass transfer, but the energy requirements for significant improvement are large [Woodle and Vilbrandt, *Am. Inst. Chem. Eng. J.,* 6, 296 (1960)].

Trice (U.S. AEC ANL-5741, 1957) used two cylindrical vessels, $T = Z$, $T = 0.10$ and 0.15 m (0.333 and 0.5 ft), through which insoluble liquid pairs were pumped. The arrangement was a form of jet mixer. The droplet size was measured by a light transmittance scheme, and for two systems, $d_p V_D \rho_C/\mu_C$ was a function of $(TV_D \rho_C/\mu_C)(TV_D^2 \rho_C/\sigma)^{2/3}\varphi_D^{0.5}$. The mass-transfer coefficient for the continuous phase in two systems k_C' was given by

$$k_C' T/D_C = 0.03(TV_D\rho_C/\mu_C)^{0.88} N_{ScC}^{0.5} \tag{21-19}$$

Injectors The flow of one liquid is induced by the flow of the other, with only the majority liquid being pumped at relatively high velocity. Figure 21-77 shows a typical device used in semibatch fashion for washing oil with a recirculated wash liquid. It is installed directly in the settling drum. See also Hampton (U.S. Patent 2,091,709, 1933), Sheldon (U.S. Patent 2,009,347, 1935), and Ng

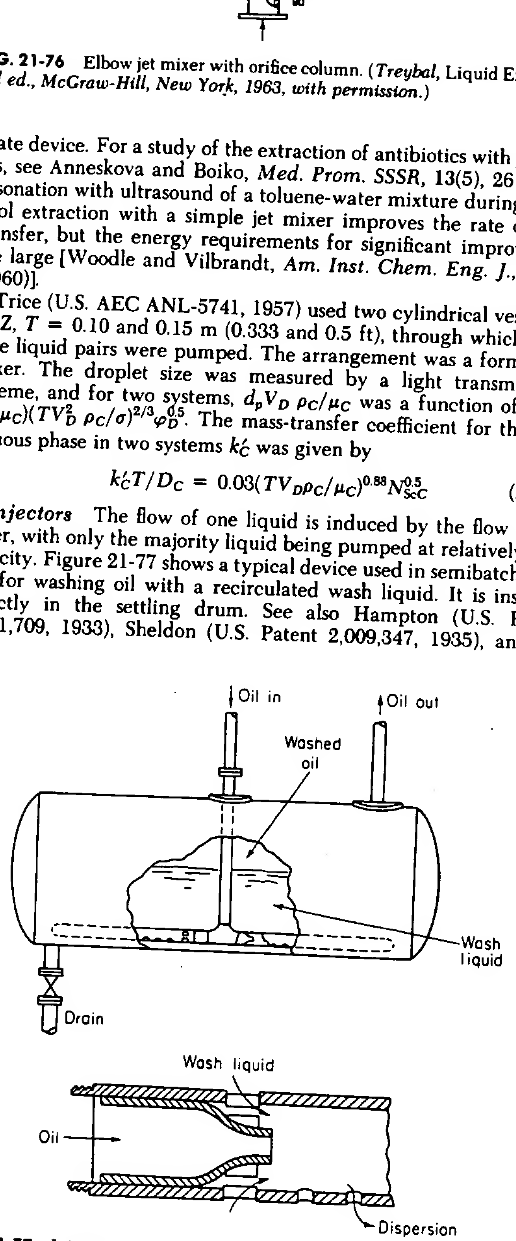

FIG. 21-77 Injector mixer. (*Ayres, U.S. Patent 2,531,547, 1950.*)

(U.S. Patent 2,665,975, 1954). Folsom [*Chem. Eng. Prog.,* 44, 765 (1948)] gives a good review of basic principles. The most thorough study for extraction is provided by Kafarov and Zhukovskaya [*Zh. Prikl. Khim.,* 31, 376 (1958)], who used very small injectors. With an injector measuring 73 mm from throat to exit, with 2.48-mm throat diameter, they extracted benzoic acid and acetic acid from water with carbon tetrachloride at the rate of 58 to 106 L/h, to obtain a stage efficiency $E = 0.8$ to 1.0. Data on flow characteristics are also given. Boyadzhiev and Elenkov [*Collect. Czech. Chem. Commun.,* 31, 4072 (1966)] point out that the presence of surface-active agents exerts a profound influence on drop size in such devices.

Orifices and Mixing Nozzles Both liquids are pumped through constrictions in a pipe, the pressure drop of which is partly utilized to create the dispersion (see Fig. 21-78). Single nozzles or several in series may be used. For the orifice mixers, as many as 20 orifice plates each with 13.8-kPa (2-lb/in²) pressure drop may be used in series [Morell and Bergman, *Chem. Metall. Eng.,* 35, 211 (1928)]. In the Dualayer process for removal of mercaptans from gasoline, 258 m³/h (39,000 bbl/day) of oil and treating solution are contacted with 68.9-kPa (10-lb/in²) pressure drop per stage [Greek et al., *Ind. Eng. Chem.,* 49, 1938 (1957)]. Holland et al. [*Am. Inst. Chem. Eng. J.,* 4, 346 (1958); 6, 615 (1960)] report on the interfacial area produced between two immiscible liquids entering a pipe (diameter 0.8 to 2.0 in) from an orifice, $\varphi_D = 0.02$ to 0.20, at flow rates of 0.23 to 4.1 m³/h (1 to 18 gal/min). At a distance 17.8 cm (7 in) downstream from the orifice,

$$a_{av} = \frac{0.179}{\sigma g_c}(C_O^2\,\Delta p)^{0.75}\left(\frac{\sigma\sqrt{g_c\rho_{av}}}{\mu_D}\right)^{0.158}\left[\left(\frac{d_t}{d_O}\right)^4 - 1\right]^{0.117}\varphi_D^{0.878} \tag{21-20}$$

where a_{av} = interfacial surface, cm²/cm³; C_O = orifice coefficient, dimensionless; d_t = pipe diameter, in; d_O = orifice diameter, in; g_c = gravitational conversion factor, (32.2 lbm · ft)/(lbf · s²); Δp = pressure drop across orifice, lbf/ft²; μ_D = viscosity of dispersed phase, lbm/(ft · s); ρ_{av} = density of dispersed phase, lbm/ft; and σ = interfacial tension, lbf/ft. See also Shirotsuka et al. [*Kagaku Kogaku,* 25, 109 (1961)].

Valves Valves may be considered to be adjustable orifice mixers. In desalting crude petroleum by mixing with water, Hayes et al. [*Chem. Eng. Prog.,* 45, 235 (1949)] used a globe-valve mixer operating at 110- to 221-kPa (16- to 32-lb/in²) pressure drop for mixing 66 m³/h (416 bbl/h) oil with 8 m³/h (50 bbl/h) water, with best results at the lowest value. Simkin and Olney [*Am. Inst. Chem. Eng. J.,* 2, 545 (1956)] mixed kerosine and white oil with water, using 0.35- to 0.62-kPa (0.05- to 0.09-lb/in²) pressure drop across a 1-in gate valve, at 22-m³/h (10-gal/min) flow rate for optimum separating conditions in a cyclone, but higher pressure drops were required to give good extractor efficiencies.

Pumps Centrifugal pumps, in which the two liquids are fed to the suction side of the pump, have been used fairly extensively, and they offer the advantage of providing interstage pumping at the same time. They have been commonly used in the extraction of

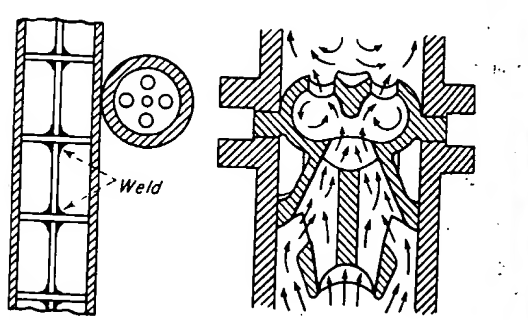

FIG. 21-78 Orifice mixer and nozzle mixer.

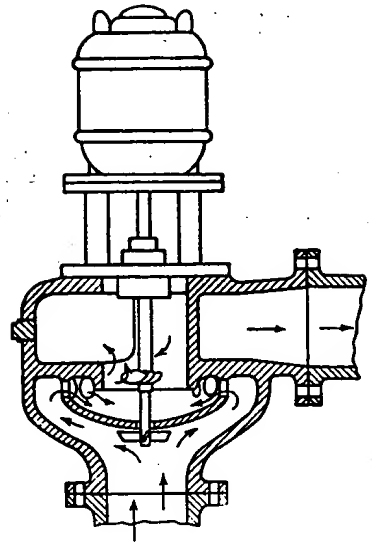

FIG. 21-79 Nettco Corp. Flomix. *(Chase, U.S. Patent 2,183,859, 1939.)*

phenols from coke-oven liquors with light oil [Gollmar, *Ind. Eng. Chem.*, **39**, 596 1947); Carbone, *Sewage Ind. Wastes*, **22**, 200 (1950)], but the intense shearing action causes emulsions with this low-interfacial-tension system. Modern plants use other types of extractors. Pumps are useful in the extraction of slurries, as in the extraction of uranyl nitrate from acid-uranium-ore slurries [*Chem. Eng.*, **66**, 30 (Nov. 2, 1959)]. Shaw and Long [*Chem. Eng.*, **64**(11), 251 (1957)] obtain a stage efficiency of 100 percent (E = 1.0) in a uranium-ore-slurry extraction with an open impeller pump. In order to avoid emulsification difficulties in these extractions, it is necessary to maintain the organic phase continuous, if necessary by recycling a portion of the settled organic liquid to the mixer.

Agitated Line Mixer See Fig. 21-79. This device, which combines the features of orifice mixers and agitators, is used extensively in treating petroleum and vegetable oils. It is available in sizes to fit ½ to 10-in pipe. The device of Fig. 21-80, with two impellers in separate stages, is available in sizes to fit 4- to 20-in pipe.

Packed Tubes Cocurrent flow of immiscible liquids through a packed tube produces a one-stage contact, characteristic of line mixers. For flow of isobutanol-water* through a 0.5-in diameter tube packed with 6 in of 3-mm glass beads, Leacock and Churchill [*Am. Inst. Chem. Eng. J.*, **7**, 196 (1961)] find

$$k_C a_{av} = c_1 L_C^{0.5} L_D \tag{21-21}$$

$$k_D a_{av} = c_2 L_C^{0.75} L_D^{0.75} \tag{21-22}$$

where c_1 = 0.00178 using SI units and 0.00032 using U.S. customary units; and c_2 = 0.0037 using SI units and 0.00057 using U.S. customary units. These indicate a stage efficiency approaching 100 percent. Organic-phase holdup and pressure drop for larger pipes similarly packed are also available [Rigg and Churchill, ibid., **10**, 810 (1964)].

Pipe Lines The principal interest here will be for flow in which one liquid is dispersed in another as they flow cocurrently through a pipe (stratified flow produces too little interfacial area for use in liquid extraction or chemical reaction between liquids). Drop size of dispersed phase, if initially very fine at high concentrations, increases as the distance downstream increases, owing to coalescence [see Holland, loc. cit.; Ward and Knudsen, *Am. Inst. Chem. Eng. J.*, **13**, 356 (1967)]; or if initially large, decreases by breakup in regions of high shear [Sleicher, ibid., **8**, 471 (1962); *Chem. Eng. Sci.*, **20**, 57 (1965)]. The maximum drop size is given by (Sleicher, loc. cit.)

$$\frac{d_{p,max}\rho_C V^2}{\sigma g_c} \sqrt{\frac{\mu_C V}{\sigma g_c}} = C\left[1 + 0.7\left(\frac{\mu_D V}{\sigma g_c}\right)^{0.7}\right] \tag{21-23}$$

where C = 43 (d_t = 0.013 m or 0.0417 ft) or 38 (d_t = 0.038 m or 0.125 ft), with $d_{p,av} = d_{p,max}/4$ for high flow rates and $d_{p,max}/13$ for low velocities.

Extensive measurements of the rate of mass transfer between n-butanol and water flowing in a 0.008-m (0.314-in) ID horizontal pipe are reported by Watkinson and Cavers [*Can. J. Chem. Eng.*, **45**, 258 (1967)] in a series of graphs not readily reproduced here. Length of a transfer unit for either phase is strongly dependent upon flow rate and passes through a pronounced maximum at an organic-water phase ratio of 0.5. In energy (pressure-drop) requirements and volume, the pipe line compared favorably with other types of extractors. Boyadzhiev and Elenkov [*Chem. Eng. Sci.*, **21**, 955 (1966)] concluded that, for the extraction of iodine between carbon tetrachloride and water in turbulent flow, drop coalescence and breakup did not influence the extraction rate. Yoshida et al. [*Coal Tar* (Japan), **8**, 107 (1956)] provide details of the treatment of crude benzene with sulfuric acid in a 1-in diameter pipe, N_{Re} = 37,000 to 50,000. Fernandes and Sharma [*Chem. Eng. Sci.*, **23**, 9 (1968)] used cocurrent flow downward of two liquids in a pipe, agitated with an upward current of air.

The pipe has also been used for the transfer of heat between two immiscible liquids in cocurrent flow. For hydrocarbon oil–water, the heat-transfer coefficient is given by

$$\frac{U a_{av} d_t^2}{v k_{to}} = \frac{\varphi_D N_{We,t}^{6/5}}{\dfrac{k_{to}}{0.415 k_{tC}} + \dfrac{k_{to}}{0.173 k_{tD}}} \tag{21-24}$$

for φ_D = 0 to 0.2. Additional data for φ_D = 0.4 to 0.8 are also given. Data for stratified flow are given by Wilke et al. [*Chem. Eng. Prog.*, **59**, 69 (1963)] and Grover and Knudsen [*Chem. Eng. Prog.*, **51**, *Symp. Ser.* 17, 71 (1955)].

Mixing in Agitated Vessels Agitated vessels may frequently be used for either batch or continuous service and for the latter may be sized to provide any holding time desired. They are useful for liquids of any viscosity up to 750 Pa·s (750,000 cP), although in contacting two liquids for reaction or extraction purposes viscosities in excess of 0.1 Pa·s (100 cP) are only rarely encountered.

Mechanical Agitation This type of agitation utilizes a rotating impeller immersed in the liquid to accomplish the mixing and dispersion. There are literally hundreds of devices using this principle,

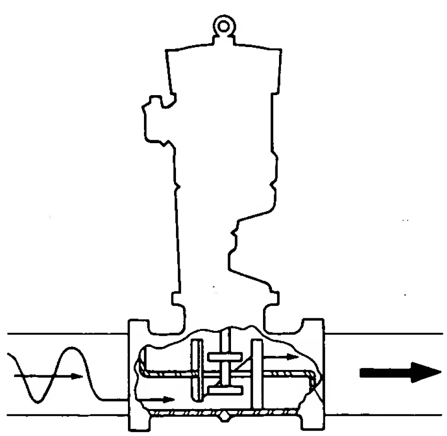

FIG. 21-80 Lightnin line blender. *(Mixing Equipment Co., Inc., with permission.)*

*Isobutanol dispersed: L_D = 3500 to 27,000; water continuous; L_C = 6000 to 32,000 in pounds-mass per hour-square foot (to convert to kilograms per second-square meter, multiply by 1.36 × 10^{-3}).